

seem to have much effect. There is no doubt, however, that the purer the neon the more brilliant is the glow, and at the same time it is more difficult to destroy the glow by shaking or electrifying the tube.

An experiment was made in a silica tube with the neon at atmospheric pressure; the glow was very much brighter than in a glass tube under the same circumstances.

*Note on the Results of Cooling certain Hydrated Platin-Cyanides
in Liquid Air.*

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In the course of Sir James Dewar's important low-temperature researches he made an interesting and significant observation with a salt which had been supplied to the Laboratory of the Royal Institution as "Lithium Platinocyanide."* When this nearly white crystallised substance was cooled in liquid air it assumed a distinct *red* colour, which did not persist at ordinary temperatures, the material resuming its usual appearance. Sir James was so good as to give the writer a portion of the salt for examination, as it seemed desirable to seek for some explanation of the remarkable colour change observed.

On repeating the above-mentioned experiment several times with one and the same portion of Sir J. Dewar's specimen it was subsequently found that the substance gradually lost the property of becoming red in liquid air, and assumed instead a marked *yellow* colour, which was retained at ordinary temperatures. This additional phenomenon has also to be explained, as it is presumably connected with that first observed.

Chemical examination of the Royal Institution specimen led to the conclusion that it was a mixture of the hydrated chloride, cyanide and sulphate of lithium with a platin-cyanogen salt of lithium, and that the proportion of the latter compound present was small.

The percentages of platinum and of lithium were directly determined in the R.I. specimen and found to be

Platinum	1·82
Lithium	9·56

* See p. 667, 'Proceedings of the Royal Institution' for 1895.

Hence the percentage of platinum *compound* present could not exceed 5 per cent. of the mixture of salts. When this specimen was examined under a microscope some minute red specks were seen, and these minute particles deepened much in tint when the material was cooled in liquid air. The general red coloration of the mass at the same time indicated that the platinum colour-producing compound was also diffused through the salts in a state of solid solution.

The separation and identification of a small amount of a platin-cyanide in much saline material is not very satisfactory, hence the method of comparison was adopted. It seemed highly probable, having regard to all the circumstances, that the question to be decided was whether the compound present was a platinocyanide or one of the much less known platinicyanides—the presumption being, of course, rather in favour of the former.

With a view to this comparison I prepared afresh some pure lithium platinocyanide and obtained the salt in fine grass-green crystals when fully hydrated. On completely analysing these crystals they gave data agreeing well with the formula



When cooled in liquid air this salt did *not* alter materially in colour—its green tint simply became paler after prolonged immersion. Even when previously diffused through hydrated lithium chloride, and the mixture cooled as before, it merely assumed a somewhat more yellow shade; but neither by cold nor heat did the pure material, or the mixture, become *red* on dehydration. It was, therefore, evident that the platinum compound present in the R.I. specimen was not a platinocyanide of lithium, and was probably a platinicyanide of the same base—the latter differing from the former in containing one more cyanogen group.

Happening to have in my collection a finely crystallised specimen of lithium platinicyanide, its exact composition was then ascertained by direct analysis, and was found to be represented by the formula



Hence the material was ready to hand for carrying out the further comparison. This compound is, however, of a full *orange red colour*, at ordinary temperatures, and when cooled in liquid air becomes a magnificent *ruby-red* which does not alter on prolonged cooling. These observations did not, at first, seem to help much toward the end in view, but a careful study of the variations in hydration of the platinicyanide cleared away all further difficulty.

The orange-red di-hydrated crystals easily dissolve in water and form

a colourless solution. When this solution is cautiously evaporated at 40° to 50° to the crystallising point and then quickly cooled to 15°, long colourless needle-like crystals separate which exhibit a slight lavender fluorescence. These crystals, when collected and quickly dried by pressure, were found to include 3H₂O, *i.e.* one more molecule of water of crystallisation than the red salt. This colourless tri-hydrate easily parts with one molecule of water and becomes the red di-hydrate either by heat or when the colourless crystals are cooled in liquid air. In the latter case, very rapid cooling always gave some yellow material in addition to the red substance, but when the reduction in temperature was carried out very slowly the red compound only was produced.

Further, when the orange-red crystals of the di-hydrated salt were very carefully heated until one of the remaining molecules of water was driven off, a yellow substance remained, which latter, if exposed to moist air, speedily resumed water and became red again. I found, however, that a persistent yellow mono-hydrate could be obtained by adding to a colourless aqueous solution of the tri-hydrate a small proportion of an indifferent but highly hydrated salt—sodium sulphate—then evaporating to dryness and gently heating the residue. The red stage of dehydration was quickly passed, and a persistent pure yellow-coloured product remained, recalling in appearance the yellow substance which results from the quick cooling of the pure substance, as noted above, and also the product of the repeated cooling and thawing of the R.I. specimen, as mentioned at the beginning of this note.

Finally, when the pure platinicyanide was sufficiently heated, the last molecule of water of crystallisation was driven off, and a white anhydrous substance remained. It is, therefore, comparatively easy to obtain the following compounds by the means above indicated:—

$\text{Li}_2\text{Pt}(\text{CN})_5^*$	White.
$\text{Li}_2\text{Pt}(\text{CN})_5\text{H}_2\text{O}$	Yellow.
$\text{Li}_2\text{Pt}(\text{CN})_5\text{H}_2\text{O}$	Orange-red.
$\text{Li}_2\text{Pt}(\text{CN})_5\text{H}_2\text{O}$	Colourless.

These variations of colour with degrees of hydration are doubtless to be connected with the differences in arrangement of the water molecules in the greater crystalline molecules, and their consequent effects on light.

The study of these hydrates evidently supplies the interpretation of the phenomena observed on cooling the Royal Institution specimen repeatedly

* These formulæ should probably be doubled, but it is unnecessary to do so here, as the simpler expressions serve equally to represent the essential variations.

in liquid air. The mixture of hydrated chloride, cyanide and sulphate of lithium used included rather less than 5 per cent. of lithium platinicyanide, which was chiefly in the tri-hydrated colourless condition. When the temperature of the mixture was reduced in liquid air, one molecule of water quickly separated, and the *red* di-hydrated salt was formed; but on warming up to the ordinary temperature, the colourless tri-hydrate was reproduced. The other hydrated lithium salts present are doubtless simultaneously dehydrated at the low temperatures reached, although these changes cannot be directly recognised as they are unaccompanied by colour alteration. In rapid cooling of the mixed (or even of the pure) material in liquid air a little of the yellow mono-hydrate is always formed and, as already noted, this rehydration of the yellow substance is singularly inhibited when neutral salts are present which are themselves avid of water, so that frequent alternations of cooling and warming gradually lead to the complete conversion of the platinum compound into the persistent yellow mono-hydrate.

The facts observed regarding the chemical changes of lithium platinicyanide hydrates not only serve to explain the phenomena noted on cooling the R.I. specimen to temperatures between -180° and -200° , but also indicate that the study of graduated dehydration of coloured salts at low temperatures may present considerable advantages, as compared with that of similar salts under the more completely disintegrating effects of heat.
